

# Microscopic study of the effect of impurities on the first order spin density wave transition in $\text{BaFe}_2\text{As}_2$

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We report an  $^{75}\text{As}$  NMR study of  $\text{BaFe}_2\text{As}_2$  in both single crystals and polycrystal forms. We find that Sn impurities in the single crystal dramatically alter the low energy spin fluctuations and suppress the ordering temperature from 138 K to 85 K. In contrast to Sn-free samples, we find that the temperature dependence of the  $^{75}\text{As}$  NMR spectra and spin lattice relaxation rates reveal a second order phase transition to a state of incommensurate magnetic order.

The newly discovered iron-based superconductors,  $\text{RFeAsO}_{1-x}\text{F}_x$  ( $\text{R}=\text{La}, \text{Sm}, \text{Ce}, \text{Nd}$ ) and the doped ternary compounds  $\text{A}_{1-x}(\text{K},\text{Na})_x\text{Fe}_2\text{As}_2$  ( $\text{A} = \text{Ba}, \text{Sr}, \text{Eu}, \text{and Ca}$ ) have stimulated interest due to their similarities to the high  $T_c$  cuprates and their surprisingly high transition temperatures ( $T_c = 55$  K) [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13]. Since these compounds do not contain the ubiquitous  $\text{CuO}_2$  planes present in the cuprate superconductors, they hold promise to shed light on some of the mysteries of high- $T_c$  superconductivity in transition metal compounds. The iron arsenides contain layers of FeAs which are presumably responsible for metallic behavior. The strongly correlated  $3d$ -electrons of the Fe experience several competing interactions that give rise to the simultaneous occurrence of a spin-density wave (SDW) instability and a structural transition from tetragonal to orthorhombic symmetry, as well as possible  $d$ -wave superconductivity [10, 14, 15]. The  $\text{AFe}_2\text{As}_2$  materials offer a unique opportunity to probe the intrinsic physics at play in these materials, because unlike the  $\text{RFeAsO}$  system, large single crystals of  $\text{AFe}_2\text{As}_2$  grow easily and therefore are ideal for investigating the anisotropy and 2-dimensional (2D) electronic character that appear important for superconductivity in the doped compounds. In this Letter, we address the role of impurities on the spin density wave transition in undoped  $\text{BaFe}_2\text{As}_2$ .

Investigations of the low energy spin dynamics of the  $\text{RFeAsO}$  materials reveal slow magnetic fluctuations associated with a continuous magnetic phase transition [16]. We find similar magnetic fluctuations present in  $\text{BaFe}_2\text{As}_2$  (Ba122), which may play a crucial role in the pairing mechanism for superconductivity [17]. However, the details of these magnetic fluctuations appear to be highly sensitive to the presence of lattice impurities. Crystals of Ba122 grown in self-flux (FeAs) have been reported to exhibit a sharp first-order like structural and magnetic phase transition at 138 K to a commensurate magnetic structure [18]. In contrast, we find that crystals grown in Sn flux exhibit a transition at 85 K that is clearly second-order and incommensurate. We argue that

random quenched Sn impurities at the level of 1% in the structure broaden the first-order transition, suppressing the ordering temperature and completely rounding the phase transition [19].

In order to investigate the microscopic properties of the Ba122 system as well as to elucidate the difference between Sn-flux grown crystals (SC) and nominally pure polycrystalline material (PC), we performed  $^{75}\text{As}$  Nuclear Magnetic Resonance (NMR) on both SC and PC samples of  $\text{BaFe}_2\text{As}_2$ . Our measurements provide unambiguous evidence for a magnetic transition at 85 K in the single crystal. On the other hand, the PC sample shows a transition at 138 K, which is consistent with earlier reports [20, 21]. We find that the low energy spin dynamics change drastically between samples, and the presence of Sn impurities in the SC lead to an incommensurate magnetic structure. The extreme sensitivity of the spin dynamics to the presence of quenched random impurities may play a crucial role in the development of superconductivity and inhomogeneity in doped samples.

Polycrystalline samples of  $\text{BaFe}_2\text{As}_2$  were prepared by first synthesizing FeAs by reacting fine Fe powder and small pieces of As in an alumina crucible in a sealed, evacuated silica ampoule. The ampoule was slowly ( $100^\circ\text{C/hr}$ ) heated to  $600^\circ\text{C}$ , soaked for 4 hours, then heated to  $700^\circ\text{C}$ , soaked for 5 hours and finally heated to  $1050^\circ\text{C}$ . That temperature was kept for 4 hours, and then the furnace was shut off. Next, a stoichiometric mixture of FeAs and Ba were placed in a Ta tube, which was sealed in an evacuated quartz ampoule. The temperature was increased to  $1050^\circ\text{C}$  at  $150^\circ\text{C/hr}$ , held at temperature for 36 hours, and then cooled to  $800^\circ\text{C}$ , where it was held for 2 days. Single crystals of  $\text{BaFe}_2\text{As}_2$  were grown in Sn flux in the ratio  $\text{Ba:Fe:As:Sn}=1:2:2:20$ . The starting elements were placed in an alumina crucible and sealed under vacuum in a quartz tube. The tube was placed in a furnace and heated to  $500^\circ\text{C}$  at  $100^\circ\text{C}$ , held at that temperature for 6 hours. This sequence was repeated at  $750^\circ\text{C}$ ,  $950^\circ\text{C}$  and at a maximum temperature of  $1100^\circ\text{C}$ , with hold times of 8 hr, 12 hr, and 4 hr, respectively. The sample was then cooled slowly

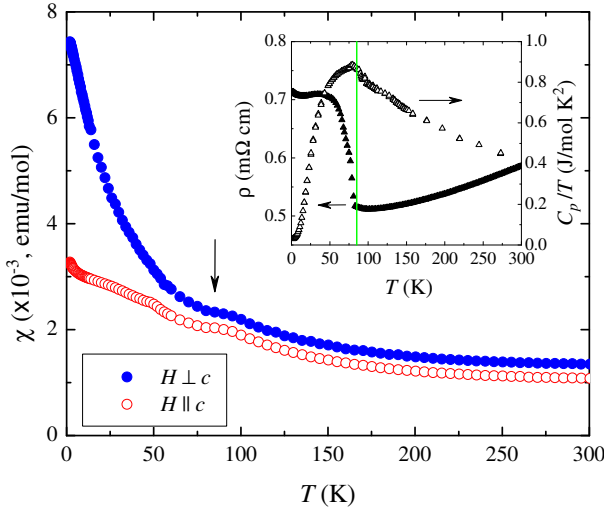


FIG. 1: Magnetic susceptibility  $\chi(T)$  measured at  $H = 0.1$  T of SC BaFe<sub>2</sub>As<sub>2</sub>. A small anomaly at 85 K (arrow) is clearly visible. Inset: Resistivity and specific heat versus temperature in the SC sample.

( $\sim 4^\circ\text{C/hr}$ ) to  $600^\circ\text{C}$ , at which point the excess Sn flux was removed using a centrifuge. The resulting plate-like crystals of typical dimensions  $3 \times 3 \times 0.1 \text{ mm}^3$  and are oriented with the  $c$ -axis normal to the plate.

Fig. 1 shows the magnetic susceptibility  $\chi(T)$  of the SC sample measured at 0.1 T. The temperature dependence and anisotropy are similar to earlier reports, as are our measurements of resistivity and specific heat [9]. The rapid increase of  $\chi$  at low temperatures indicates the presence of a small amount of an impurity phase, which was not detectable in powder X-ray spectra. Relative to observations in Ref. [9], the impurity contribution to  $\chi$  is reduced by about 30 % and, as a result, a small anomaly at 85 K is clearly visible, suggesting a magnetic phase transition. We point out that the  $\chi(T)$  in the PC [20] and SC samples grown in FeAs flux [22] actually decreases slowly at high temperatures, and exhibit a clear drop at 140 K. The relatively large impurity contribution at low temperatures in our case, however, makes it difficult to obtain  $\chi(T)$  of the pure Ba122 phase. On the other hand, the As Knight shift,  $K$ , probes microscopically the intrinsic susceptibility of the Ba122. We find, in fact, that  $K$  decreases with decreasing temperature (Fig. 1) as observed in other iron arsenide materials.

Fig. 2 (a) presents the  $^{75}\text{As}$  ( $I = 3/2$ ) NMR spectra of BaFe<sub>2</sub>As<sub>2</sub> at 120 K, measured at constant frequency  $f = 45$  MHz. The spectrum shows the central ( $I_z = +\frac{1}{2} \leftrightarrow -\frac{1}{2}$ ) transition, plus two satellite peaks split by the quadrupolar interaction of the As nucleus with the local electric field gradient (EFG). We find that the quadrupolar frequency  $\nu_Q = 3eQV_{zz}/2I(2I-1)\hbar = 3(0.1) \text{ MHz}$ , where  $Q$  is the quadrupolar moment and  $V_{zz}$  is the EFG. Surprisingly, this value is 3–4 times smaller

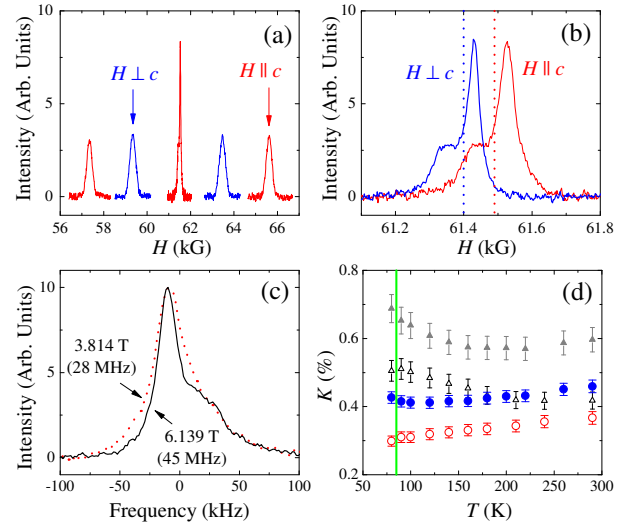


FIG. 2: (a) Full  $^{75}\text{As}$  NMR spectra at a fixed frequency of 45 MHz and at 120 K. The satellite peaks (blue lines for  $H \perp c$  and red lines for  $H \parallel c$ ) are equally spaced. For simplicity, we omit the central line for  $H \perp c$  which is 0.1 kG off from the central line for  $H \parallel c$ . (b) Central lines for both  $H \perp c$  and  $H \parallel c$ . The vertical dotted lines represent the midpoint between the satellites. (c) Comparison of spectra in the SC sample for two different fields ( $H \perp c$ ) at 220 K. (d) The Knight shift of the primary (red, blue) site and the secondary site (gray) versus temperature. The solid (open) gray triangles correspond to  $H \perp c$  ( $H \parallel c$ ), and the vertical green line at 85 K corresponds to  $T_N$ .

than observed in the LaFeAsO compounds, but is consistent with other NMR reports in BaFe<sub>2</sub>As<sub>2</sub> [15, 16, 18, 23]. The spectra of the central transition clearly reveal a narrow peak with approximately 60% of the total signal intensity, and a second broader peak consisting of  $\sim 40\%$  of the intensity. The two peaks arise from As nuclei in different local charge (EFG) or magnetic environments. In order to test whether the two peaks arise from different EFGs, we compare two spectra at different fields, since the second order shift to the central transition frequency varies as  $\nu_Q^2/H$  for  $H \perp c$  [24]. As shown in Fig. 2(c), the linewidth of the primary resonance increases with decreasing  $H$ , whereas the secondary peak at higher frequency is poorly resolved at the lower field, suggesting no significant quadrupolar shift of this site. This result suggests that the primary peak experiences an EFG and is associated with the intrinsic Ba122 phase and the secondary peak arises from As with little or no EFG. Furthermore, we find that the two peaks have vastly different magnetic shifts [Fig. 2(d)]. A plausible scenario, then, is that the secondary peak arises from an impurity phase containing As, whereas the primary peak arises from the BaFe<sub>2</sub>As<sub>2</sub> phase, and probes the intrinsic physics of this material.

The central line of  $^{75}\text{As}$  NMR ( $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ ) and its temperature dependence are shown in Fig. 3(a) and (b).

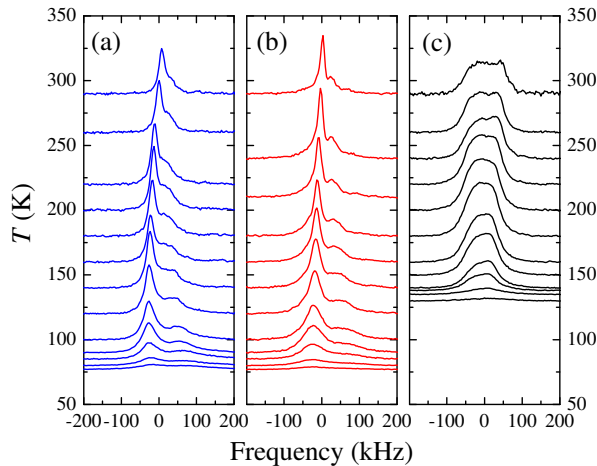


FIG. 3:  $^{75}\text{As}$  NMR spectra of the central transition in  $\text{BaFe}_2\text{As}_2$  for both the SC and PC samples at 45 MHz for the case of : (a)  $H \perp c$  at 6.139 T, (b)  $H \parallel c$  at 6.149 T, and (c) the polycrystal sample at  $H = 6.148$  T. Two peaks are clearly distinguished in the SC. Below the ordering transition, the spectra quickly broaden and the signal is drastically reduced.

Spectra measured on the PC sample [Fig. 3(c)] reflect the Knight shift broadening expected for a randomly oriented powder. For the SC sample, we observe gradual broadening of spectra down to 85 K and much faster broadening below 85 K. This is a clear indication of a magnetic phase transition to an incommensurate state. These data are consistent with a picture in which the internal field felt by As nuclei is distributed spatially, giving rise to an inhomogeneous broadening of the  $^{75}\text{As}$  NMR line. This observation contrasts with recent neutron scattering results and NMR in self-flux crystals of  $\text{BaFe}_2\text{As}_2$  and  $\text{SrFe}_2\text{As}_2$  that reveal commensurate order with  $\mathbf{Q} = (1, 0, 1)$  [18, 21, 25]. In the PC sample, we find that below 138 K the spectra also broaden, showing no evidence for a commensurate magnetic order. However, in this case the spectra should be broadened anyway due to the strong angular dependence of the resonance frequencies in the polycrystalline sample [26].

It is noteworthy that the spectra of the SC for both orientations do not show any discontinuities through  $T_N$ . This observation contrasts with NMR measurements in self-flux grown  $\text{BaFe}_2\text{As}_2$  and  $\text{CaFe}_2\text{As}_2$  crystals [18, 27]. In these cases, the EFG changes discontinuously at the structural transition, and is reflected in the second order corrections to the central transition frequency. Our observations in the Sn-flux grown crystal suggest there is no change in the structure down to 85 K. Below this temperature, the broad, incommensurate magnetic order preclude any detailed analysis of the EFG through the NMR spectra.

In order to probe the low energy spin dynamics, we

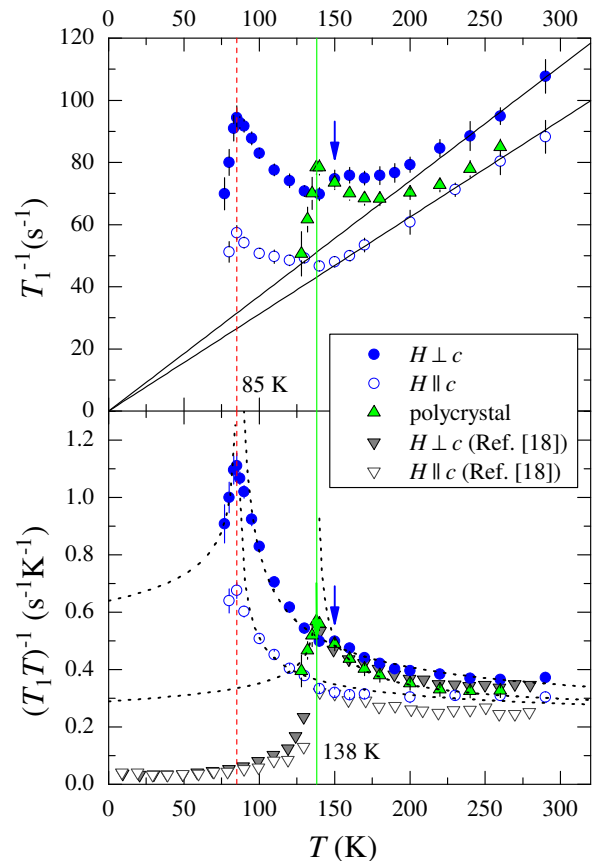


FIG. 4: (a)  $T_1^{-1}$  versus  $T$  in  $\text{BaFe}_2\text{As}_2$  at 45 MHz for field along  $c$  and in the  $ab$  plane. The dotted red line at 85 K indicates the second order transition (disordered sample) and the solid green line at 138 K indicates the first order transition (pure sample). An additional weak maximum at 150 K is evident only for  $H \perp c$ . The solid lines are guides to the eye. (b)  $(T_1 T)^{-1}$  versus  $T$ . The dotted curves are fits as described in the text, and the gray data points are reproduced from [18].

have measured the spin lattice relaxation rate,  $T_1^{-1}$ , as a function of temperature [Fig. 4(a)] for both SC and PC samples. At high temperatures,  $(T_1 T)^{-1}$  [Fig. 4(b)] approaches a constant as expected for metallic systems. As the temperature decreases,  $(T_1 T)^{-1}$  increases to a maximum at  $T_N = 85$  K for the SC (135 K for the PC), and drops rapidly below these temperatures. This behavior is similar to  $^{139}\text{La}$  NMR results on  $\text{LaFeAsO}$  at  $T_N = 142$  K [16] and  $^{75}\text{As}$  NMR on polycrystal  $\text{BaFe}_2\text{As}_2$  [26], implying that the parent compounds of superconducting materials are governed by similar magnetic properties. The strong temperature dependence above  $T_N$  reflects the critical slowing down of spin fluctuations above a second order phase transition, and the rapid drop below  $T_N$  reflects the opening of the gap associated with an SDW instability. The dotted lines in Fig. 4 show fits to the self-consistent renormalization (SCR) theory for

weak itinerant antiferromagnets:

$$\frac{1}{T_1 T} = \begin{cases} a + b/\sqrt{T - T_N} & (T > T_N) \\ c(1 - T/T_N)^{-\beta} & (T < T_N), \end{cases} \quad (1)$$

where we have fixed the critical exponent for the order parameter,  $\beta = 0.15$ , as measured by Nakai et al. [16, 28]. Here we find  $a = 0.18 \text{ (sK)}^{-1}$ ,  $b = 2.45 \text{ s}^{-1}\text{K}^{-1/2}$  and  $c = 0.64 \text{ (sK)}^{-1}$  for  $H \perp c$ ;  $a = 0.22 \text{ (sK)}^{-1}$ ,  $b = 1.0 \text{ s}^{-1}\text{K}^{-1/2}$ , and  $c = 0.29 \text{ (sK)}^{-1}$  for  $H \parallel c$ ; and  $a = 0.2 \text{ (sK)}^{-1}$ ,  $b = 1.2 \text{ s}^{-1}\text{K}^{-1/2}$ , and for the PC sample. These values are roughly one order of magnitude larger than those reported for LaOFeAs [16]. We note that the 2D character of the fluctuations is clearly reflected in different  $b$  values for the two orientations. It is not clear if the difference arises from the anisotropy of the hyperfine interaction itself, or rather in the intrinsic 2D fluctuations of the electronic system.

The striking feature in the spin lattice relaxation data is the absence of any discontinuity associated with a first order transition. Recent NMR measurements in a single crystal of BaFe<sub>2</sub>As<sub>2</sub> grown by FeAs flux show a drop in  $T_1^{-1}$  at  $T_N = 135 \text{ K}$  [18]. In contrast, for crystals grown in Sn-flux, the structural and magnetic transition is suppressed to 85 K. We find that in this case, the phase transition is no longer first order, but suggestive of a continuous second order one. The  $T_1^{-1}$  data for both samples agree at high temperature, but clearly deviate below 135 K. In the Sn-flux grown samples,  $T_1^{-1}$  increases down to 85 K, representing the growth of slow antiferromagnetic fluctuations associated with the *second order* transition at 85 K. Since Sn-flux grown samples are believed to contain Sn substitutions for As at the level of  $\sim 1 \%$ , we conclude that these Sn impurities dramatically affect the first order transition [9]. (Note that these impurities are present in the primary BaFe<sub>2</sub>As<sub>2</sub> phase, and the effect is unrelated to the 40 % extrinsic secondary phase discussed above.) Not only do the impurities suppress the ordering temperature by nearly 40%, they also round out the transition and alter the critical dynamics [19, 29]. At a first order transition in the presence of disorder, local fluctuations of the ordered phase may be destabilized because of the high cost of forming phase boundaries. Consequently the ordering temperature of the entire system can be suppressed, and the discontinuity in the order parameter can be smeared out. We suggest that the sensitivity of BaFe<sub>2</sub>As<sub>2</sub> to Sn impurities represents a generic aspect of the FeAs plane, and that similar effects may be at play in the LaOFeAs materials. This smearing out effect may explain the strong increase in the order parameter and the unusual  $\beta = 0.15$  exponent observed in the ordered state of LaOFeAs [16, 30]. Furthermore, recent  $\mu$ SR experiments suggest that the transition between an SDW ground state and a superconducting one upon F doping is first order in LaOFeAs [31], although

there has been some report of coexisting SDW and superconductivity for intermediate dopings [32, 33].

The dramatic temperature dependence of  $T_1^{-1}$  above  $T_N$  reflects the critical slowing down of the spin fluctuations [34]. If the magnetic transition is indeed smeared out by impurities, the critical dynamics of this transition may not be universal, but rather are determined by the extrinsic effect of the Sn impurities. Nevertheless, these slow magnetic dynamics may play an important role in the emergence of superconductivity under pressure in the AF<sub>2</sub>As<sub>2</sub> compounds, or in F-doped LaOFeAs [17].

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- [1] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, *J. Am. Chem. Soc.* **130**, 3296 (2008).
  - [2] H. Takahashi et al., *Nature* **453**, 376 (2008).
  - [3] X. H. Chen et al., *Nature* **453**, 761 (2008).
  - [4] L. Ding et al., *Phys. Rev. B* **77**, 180510(R) (2008).
  - [5] Z.-A. Ren et al., *Chin. Phys. Lett.* **25**, 2215 (2008).
  - [6] Z.-A. Ren et al., *Europhys. Lett.* **82**, 57002 (2008).
  - [7] G. F. Chen et al., *Phys. Rev. Lett.* **100**, 247002 (2008).
  - [8] M. Rotter, M. Tegel, and D. Johrendt, *Phys. Rev. Lett.* **101**, 107006 (2008).
  - [9] N. Ni et al., *Phys. Rev. B* **78**, 014507 (2008).
  - [10] G. Wu et al., arXiv:0806.4279 (2008).
  - [11] K. Sasmal et al., *Phys. Rev. Lett.* **101**, 107007 (2008).
  - [12] G. F. Chen et al., *Chin. Phys. Lett.* **25**, 3403 (2008).
  - [13] F. Ronning et al., *J. Phys.: Cond. Matt.* **20**, 322201 (2008).
  - [14] Q. Si and E. Abrahams, *Phys. Rev. Lett.* **101**, 076401 (2008).
  - [15] H.-J. Grafe et al., *Phys. Rev. Lett.* **101**, 047003 (2008).
  - [16] Y. Nakai et al., *J. Phys. Soc. Jpn.* **77**, 073701 (2008).
  - [17] P. Monthoux, D. Pines, and G. G. Lonzarich, *Nature* **450**, 1177 (2007).
  - [18] K. Kitagawa et al., arXiv:0807.4613 (2008).
  - [19] Y. Imry and M. Wortis, *Phys. Rev. B* **19**, 3580 (1979).
  - [20] M. Rotter et al., *Phys. Rev. B* **78**, 020503(R) (2008).
  - [21] Q. Huang et al., arXiv:0806.2776 (2008).
  - [22] X. F. Wang et al., arXiv:0806.2452 (2008).
  - [23] H. Mukuda et al., *J. Phys. Soc. Jpn.* **77**, 093704 (2008).
  - [24] C. P. Slichter, *Principles of Magnetic Resonance* (Springer-Verlag, Berlin, 1990).
  - [25] A. Jesche et al., arXiv:0807.0632 (2008).
  - [26] H. Fukazawa et al., *J. Phys. Soc. Jpn.* **77**, 093706 (2008).
  - [27] S.-H. Baek et al., arXiv:0808.0744 (2008).
  - [28] T. Moriya, *Spin Fluctuations in Itinerant Electron Magnetism* (Springer-Verlag, Berlin, 1985).
  - [29] A. J. Millis, *Solid State Comm.* **126**, 3 (2003).
  - [30] H.-H. Klauss et al., *Phys. Rev. Lett.* **101**, 077005 (2008).
  - [31] H. Luetkens et al., arXiv:0806.3533 (2008).
  - [32] A. J. Drew et al., *Phys. Rev. Lett.* **101**, 097010 (2008).
  - [33] H. Chen et al., arXiv:0807.3950 (2008).
  - [34] N. J. Curro et al., *Nature* **434**, 622 (2005).